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THE DETERMINATION OF DISSOLVED OXYGEN BY THE RIDEAL STEWART AND ALSTERBERG MODIFICATIONS OF THE WINKLER METHOD.

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Among the many modifications of the Winkler method advocated for the determination of dissolved oxygen in the presence of nitrite, probably the most widely used is the Rideal-Stewart method. It has been recognized for some time, however, that in the presence of organic matter this modification gives low results. Consequently other modifications have been proposed. Noll(1) proposed the use of urea for the destruction of nitrites but as Alsterberg(2) has pointed out, its use requires a long period of contact (approximately twenty-four hours) and is, therefore, impracticable. Alsterberg substituted sodium azide for urea and found that the destruction of nitrite could be accomplished in a few minutes. Ohle(3) in a summary of methods used for the determination of dissolved oxygen in the presence of nitrite does not consider the azide method important. However, as pointed out by Brandt(4) this modification has been used quite extensively in Germany on river studies.

In the course of some previous work(5) on the determination of the solubility of oxygen in sewage, a number of modifications of the Winkler method were used. This work has since been extended to include the azide modification. The results obtained were so promising that it was decided to make a comparative

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study of the sodium azide and Rideal Stewart modifications during the course of a survey of the Scioto River. The results obtained by these two methods on samples from this polluted stream are given in the present paper.

Experimental Methods

In this study the samples of water were collected from regular sampling stations distributed along the Scioto River from 3 to 115 miles from Columbus, Ohio. The samples of water that were to be used for comparative dissolved oxygen determinations by the two methods were obtained simultaneously in two standard 300 ml. bottles contained in one standard sampling apparatus for collecting samples for dissolved oxygen determinations. All samples were tightly stoppered and immediately transported by automobile to a central laboratory at Chillicothe, Ohio, for analysis upon arrival.

The Rideal Stewart (permanganate) procedure as given in the present edition of Standard Methods(6) was used on one series of samples. On the series of duplicate samples the sodium azide procedure was used to destroy the nitrite contained therein. However, the sodium azide procedure of Brandt (loc. cit.) was reversed. That is, the nitrite was destroyed in acid solution before the Winkler procedure and consequent liberation of iodine in order that the free iodine might not react with any organic matter present during the time interval allowed for nitrite destruction and thus tend to give low results. The following procedure was found to be entirely satisfactory even though the nitrite concentration might be as high as 4.0 p.p.m.

To the sample of water in a standard 300 ml. bottle, 0.7 ml. of concentrated H_2SO_4 followed by 0.8 ml. of a 2.0 per cent aqueous solution of sodium azide is added. The bottle is stoppered, the contents are mixed by shaking and the bottle is allowed to stand for ten minutes. One (1) ml. of manganous sulfate solution and 3.0 ml. of alkaline potassium iodide solution are next added and the sample is shaken for twenty seconds. Following this the precipitate is allowed to settle and the sample is acidified with 2.0 ml. of concentrated H_2SO_4. The liberated iodine on a volume of solution equivalent to 200 ml. of the original sample is titrated immediately with N/40 sodium thiosulfate using starch indicator.

The ten minute interval of standing after mixing the sodium azide solution with the acidified sample is necessary for the completion of the azide nitrite reaction and destruction of the nitrite.

Analytical Results.

Four hundred and eleven pairs of duplicate samples of water from the Scioto River have been analysed by the two methods described. Table 1 gives the mean 5-day B.O.D. and the nitrite range encountered at the sampling points during the period of investigation. These data show that the mean 5-day B.O.D. ranged from 2.63 p.p.m. at Columbus above the sewer outlets to 12.39 p.p.m. at Shadeville, the point of maximum pollution. Each figure represents the mean of the results from 40 or more individual samples collected at two day intervals during this period. The nitrite

nitrogen range obtained during this period is quite wide, and it is apparent that some method for destroying the nitrite must be used before the Winkler method for dissolved oxygen is applicable.

The dissolved oxygen results obtained by both methods on all of the samples arranged according to sampling stations are presented in Table 2. These data indicate that the sodium azide modification gives slightly higher average results than the Rideal Stewart modification. The actual mean differences in dissolved oxygen are not great at Shadeville, Commercial Point and South Bloomfield where the dissolved oxygen values are low and the B.O.D. values are highest. The percentage deviations are greatest, however, at these points. The mean difference between the sodium azide results and the Rideal Stewart results increased to about 0.3 p.p.m. at some of the lower stations where the dissolved oxygen content is higher. These results do not suggest any correlation between the mean B.O.D. at a station and the mean deviation of the dissolved oxygen results obtained by these methods.

To determine whether the dissolved oxygen content had any influence upon the mean deviations between the results by these methods all of the results were arranged into groups on the basis of the dissolved oxygen found by the sodium azide method as shown in Table 3. The results of this arrangement seem to suggest that the quantity of oxygen present affects the mean deviation between the results obtained by these methods. When all the results are included the mean deviations tend to increase with the dissolved

oxygen of the samples at least until an oxygen content of 7.0 p.p.m. is reached.

The frequency at which deviations of various magnitudes between the results by these methods occur for the groups of samples at each dissolved oxygen range given in Table 3 have been determined and are presented in Table 4. These data indicate that in the great majority of samples the oxygen content found by the azide modification will be higher than that found by the Rideal Stewart modification. With samples containing more than 1.0 p.p.m. of oxygen higher results were obtained with the Rideal Stewart modification on only about 5.0 per cent of the samples. These data indicate that the frequency of greater negative deviations by the Rideal Stewart method tends to increase as the dissolved oxygen content of the samples increase. This is illustrated by the plot of the deviation frequency shown in Figure 1.

Discussion.

The results obtained by the two methods check surprisingly well on the Scioto River. As it has been shown[7][8] that the Rideal Stewart modification tends to give low results in the presence of stale sewage and other forms of organic matter, it seems reasonable to ascribe the predominant negative deviations obtained by this modification to adsorption of oxygen by the organic matter during the permanganate treatment.

The sodium azide modification is very effective in nitrite destruction. The paucity of times that the starch iodine color

returns at the end point of the titration is evidence of this effectiveness. Of the 411 determinations made by this method, a return of color after titration was noted only once. In the presence of high nitrite concentration (4.0 p.p.m. or more) the manganous hydroxide floc tends to rise in the bottle. However, if the bottle is shaken the second time the nitrogen will be disengaged and the floc will settle satisfactorily. The azide method is one operation shorter than the Rideal Stewart method in that it is unnecessary to destroy the excess azide, whereas with the Rideal Stewart method it is necessary to destroy the excess permanganate with oxalate. This step often causes difficulties because either starting the Winkler procedure before all color has disappeared or adding an excess of oxalate introduces errors.

As the azide method has advantages in technique, is effective in destroying nitrite and seems less affected than the permanganate treatment by organic matter it would seem very desirable in dissolved oxygen studies. The results obtained in this study suggest that the method can be successfully applied to the determination of the dissolved oxygen content of sewage polluted streams where nitrite is encountered. Additional study of the method seems desirable in connection with biochemical oxygen demand studies where nitrite is produced during the incubation period.

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TABLE 1.

BIOCHEMICAL OXYGEN DEMAND AND NITRITE CONTENT OF THE SCIOTO RIVER WATER SAMPLES USED IN COMPARATIVE STUDY OF DISSOLVED OXYGEN METHODS.

Sampling Point	Miles from Columbus	5-day B.O.D. P.P.M.(1)	Nitrite Nitrogen Range - P.P.M.	
			Min.	Max.
Columbus	3	2.63	0.0	0.48
Shadeville	13	12.39	Tr.	1.25
Commercial Point	17	7.12	0.04	0.75
South Bloomfield	23	5.47	0.07	1.0
Red Bridge	30	4.26	0.05	0.8
Circleville	33	3.47	0.05	0.5
Penn. R.R. Bridge	35	6.04	Tr.	0.5
Kellenberger	46	4.88	0.05	0.5
Chillicothe	61	4.85	0.0	0.15
Kilgore	67	4.45	0.0	0.15
Higby	76	4.31	0.0	0.05
Waverly	92	3.64	0.0	0.05
Lucasville	115	3.49	0.0	0.05
Paint Creek (2)		6.41	Tr.	0.35

(1) Mean for May, June and July.

(2) This tributary discharges into the Scioto River below Chillicothe, Ohio.

TABLE 2.

COMPARISON OF DISSOLVED OXYGEN RESULTS ON 411 SCIOTO RIVER SAMPLES OBTAINED BY THE SODIUM AZIDE AND RIDEAL STEWART MODIFICATIONS OF THE WINKLER METHOD.

Sampling Station	No. of Samples	Mean D.O. - P.P.M.		
		Sodium Azide Mod.	Rideal Stewart Mod.	Deviation
Columbus	38	7.50	7.26	0.24
Shadeville	39	3.16(1)	2.94(1)	0.22
Commercial Point	38	3.11(2)	2.91(2)	0.20
South Bloomfield	42	2.42	2.23	0.19
Red Bridge	38	3.47	3.34	0.13
Circleville	38	4.53	4.34	0.19
Penn. R.R. Bridge	38	4.44	4.10	0.34
Kellenberger	23	4.51	4.23	0.27
Chillicothe	13	6.54	6.20	0.34
Kilgore	10	6.36	6.10	0.26
Higby	13	6.44	6.16	0.28
Waverly	10	7.32	7.04	0.28
Lucasville	10	7.60	7.37	0.27
Paint Creek	22	7.38	7.10	0.28
Miscellaneous	39	6.93	6.63	0.30

(1) 13 samples were 0.0 by each method and were not included in this average.

(2) 6 samples were 0.0 by each method and were not included in this average.

TABLE 3.

COMPARISON OF DISSOLVED OXYGEN RESULTS ON 411 SCIOTO RIVER SAMPLES OBTAINED BY THE SODIUM AZIDE AND THE RIDEAL STEWART MODIFCATIONS OF THE WINKLER METHOD

(Results arranged in groups on basis of D.O. content found by the Azide modification).

D. O. Range of Group P.P.M.	No. of Samples	Mean D.O. - P.P.M.		Mean Deviation P.P.M.
		Azide Mod.	R-S Mod.	
0.0	19	0.0	0.0	0.0
0.27 to 0.99	6	0.53	0.46	0.07
1.0 to 2.99	70	2.17	2.03	0.14
3.0 to 4.99	140	4.15	3.85	0.30
5.0 to 6.99	98	6.03	5.70	0.33
Over 7.0	78	8.42	8.11	0.31

TABLE 4.

DEVIATION FREQUENCY BETWEEN D.O. RESULTS FOUND BY THE SODIUM AZIDE MODIFICATION AND THE RIDEAL STEWART MODIFICATION ARRANGED IN GROUPS ACCORDING TO DISSOLVED OXYGEN CONTENT.

Range of D.O. content in groups.	Deviation frequency of Rideal Stewart D.O. Results from Sodium Azide Modification D.O. Results in the Stated Deviation Groups.										
	+0.31 & higher	+0.30 to +0.21	+0.20 to +0.11	+0.10 to 0.00	0.00 to -0.10	-0.11 to -0.20	-0.21 to -0.30	-0.31 to -0.40	-0.41 to -0.50	-0.51 to -0.75	Under -0.76
0.27-0.99				16.67	50.00	33.33					
1.00-2.99			2.90	5.80	39.13	24.63	20.29	2.90	2.90	1.45	
3.00-4.99	0.71			3.57	10.71	22.86	25.00	24.29	9.29	3.57	
5.00-6.99				1.02	3.06	9.18	35.71	28.57	15.31	6.12	1.02
Over 7.00		1.28		1.28	7.69	14.10	26.92	29.49	10.26	8.97	